Kinetic regimes of polyelectrolyte exchange between the adsorbed state and free solution

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We studied the exchange between the adsorbed state and free solution when polyelectrolyte chains, adsorbed to a solid surface of opposite charge, were displaced by chains of higher charge density. Metastable states of surface composition were extremely long-lived (>2–3 days). The system was a family of poly(1,4 vinyl)pyridines (PVP) with different fractions of charged segments (14%, 48%, and 98% quaternized and the same degree of polymerization); samples were exposed sequentially from aqueous D_2O solution to a single silicon oxide substrate at pH where the surface carried a large negative charge (pH$=9.2$ or 10.5). Measurements were based on Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR). As a first conclusion, we found charge of adsorbed polymer to be conserved during extended exchange times, suggesting that charge at the surface (not mass adsorbed) regulated the dynamics of adsorption and desorption. Except at the highest ionic strength charge of polymer at the surface during the displacement process considerably exceeded that for the initially-adsorbed layer, suggesting an intermediate state in which newly-adsorbed chains were more extended from the surface and not yet equilibrated in their conformations. Second, we concluded that desorption was the rate-limiting step in adsorption–desorption, since the desorption rate responded more to changes of ionic strength than did the adsorption rate onto previously-adsorbed polymer. Ionic strength appeared to modulate the intensity of sticking to the surface. Third, we found that the initial stages of desorption obeyed a simple functional form, exponential in the square root of elapsed time. This is conclusively slower than a first-order kinetic process and suggests that desorption in this polyelectrolyte system was diffusion-controlled during the initial stages. It is the same functional form observed for flexible polymers in nonpolar solvents. Fourth, we concluded that at relatively low concentration of salts desorption proceeded in two stages; one subpopulation of adsorbed chains desorbed relatively quickly, with a rate exponential in the square root of time, and a second subpopulation was so much slower to be desorb that it appeared to be kinetically frozen at the surface. The higher the ionic strength, the less the polymer was kinetically frozen and this effect disappeared entirely for the highest ionic strength. The interpretation that the kinetically-frozen states reflected conformational heterogeneities within the adsorbed layer was supported by direct measurements of the dichroic ratio of adsorbed pyridinium rings. Finally, a new kinetic regime was observed at the highest salt concentrations, in which the exchange was inhibited by worsened solubility of the displaced molecules. It is significant that this regime began at salt concentrations significantly below the point of bulk insolubility. Since most organic polyelectrolytes may be considered to be a copolymer of polar charged units and hydrophobic uncharged units, this effect is expected to be general. © *1998 American Institute of Physics.* [S0021-9606(98)51940-X]

I. INTRODUCTION

The reliable prediction of surface composition when charged macromolecular chains adsorb to solid surfaces of opposite charge is not yet possible. The preceding paper[1] established the feasibility of using Fourier transform infrared spectroscopy (FTIR) in the mode of attenuated total reflection (ATR) to study these questions. The infrared technique was found to give quantitative information not just about the total mass adsorbed, but also about the surface concentration of individual components within a mixture. By this method, *in situ* kinetic measurements of the surface composition can be made repetitively, at the same solid surface, over periods up to 2–3 days. The dependence of the mass adsorbed and chain flattening on surface charge density and on salt con-

centration were studied for adsorption onto an initially-bare solid surface. Here we follow a different experimental approach—we probe the exchange dynamics between the adsorbed state and free solution.

Apart from a few pioneering studies,[2–5] little is known yet quantitatively about this from direct experiment. Most of the rate measurements that one finds are qualitative, made to determine the time necessary to reach steady-state levels of the mass adsorbed.[6–8] There are at least three motives for seeking to understand the passage from one state to another. One is to understand surface motions and relaxations; this is important in applied science, where the use of adsorbed polyelectrolytes is ubiquitous. Practical ramifications of these questions have additional obvious implications for nu-

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merous industrial processes, among them the stabilization and flocculation of colloidal dispersions, coating of fibers in paper industries, waste-water treatment, mineral processing, and chromatographic separations. There are also obvious connections to understanding the physics of charged biomolecules, charged proteins, and nucleic acids, and ramifications in applications such as blood clotting and immunoadsorption.

Second it is important for scientific reasons to understand polyelectrolyte surface films and their mobility. One may expect that polyelectrolyte chains will crawl about on a surface. At what rate does this occur and on what does it depend? What is the mechanism of mobility? How long does it take to achieve equilibrium when the conditions that surround an adsorbed layer are altered? Entanglement effects, which dominate long-range diffusion in unbounded spaces for molecules, have been proposed in nonpolar solvents to play an even more prominent effect on the surface mobility of uncharged polymers;[9] do they likewise play a dominant role for polyelectrolytes? Intuition concerning uncharged polymers is difficult to extend to charged systems.

A third motive is to firmly assess the conditions for reversibility or irreversibility in the adsorption process. The conditions are not yet known under which it is appropriate to make the common assumption of equilibrium configurations at the state of lowest free energy (as we will see from experiments described below, the segmental sticking energy appears to be higher than is typical of weakly-adsorbing nonpolar polymers). By exploring the rate of passage from one adsorption state to another, one may seek to gain understanding about the energy barriers that separate various equilibrated or metastable states.

Large parts of the relevant literature address these issues peripherally, being concerned primarily to determine the contact time needed to reach steady-state levels of adsorption. Other relevant literature concerns protein adsorption[10,11] and is difficult to generalize to flexible chains. To summarize the picture that has emerged, the main features appear to be the following:

(1) Desorption of adsorbed chains, when solution is replaced by the same pure solvent, is commonly minimal, exceedingly slow, and insensitive to temperature. It seems that the activation energy to peel all segments off the surface at once is prohibitively high.

(2) Exchange is considerably faster between the adsorbed state and a finite concentration in free solution. This produces considerable fractionation between surface and solution, as certain molecular weight components adsorb preferentially. It seems that exchange can proceed piecemeal, a few segments at a time, with lesser activation energy associated with this cooperative process. Times for these displacement processes are nonetheless long, on the order of hours to days.

(3) Uncertainties of homogeneity of the surfaces make it difficult to come to grips with universal features of these problems. The surfaces used in various experiments have been diverse. Usually they have been colloidal in character, and therefore in principle heterogeneous topo-

graphically in addition to chemically. Polymer–solvent systems have generally been far better characterized than the solid surfaces.

(4) Comparison between polyelectrolyte surface mobility and that of uncharged polymers is little-studied from the experimental point of view. Two peculiarities of polyelectrolyte systems are evident in principle, however. First, aspects of the electrical double layer and charge screening must come into play. Second, the small-molecule ions that determine the pH and that comprise the aqueous salt solution may adsorb competitively with the polyelectrolyte.

From exchange studies of uncharged flexible polymers in hydrocarbon solvents, this laboratory has previously proposed generalizations regarding the kinetic laws that determine the kinetics of adsorption and desorption.[9,12,13] A rich kinetics was also found to be associated with presence of shear flow of solvent or polymer solution past an adsorbing surface.[14,15] In this study, avoiding the complications of shear flow, we examine rates of adsorption and desorption for a common aqueous polyelectrolyte, quaternized poly(1,4 vinyl)pyridine (PVP). Elsewhere we will consider polyelectrolyte adsorption onto *responsive* surfaces; flexible surfaces comprised of tethered polyelectrolyte chains with opposite electrical charge from that of the adsorbing moieties.

II. EXPERIMENT

The infrared methods of Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR) to measure adsorption of quaternized poly(vinylpyridine) (PVP), and the controlled oxidation of a silicon crystal to form the adsorption substrate, were described elsewhere.[16,17] The experiments were carried out at 25 °C.

Anionically polymerized poly(1,4 vinyl)pyridines (PVP) were purchased from Polymer Source, Quebec, Canada. The samples, synthesized by anionic polymerization, were characterized (according to manufacturer's specifications) by a degree of stereoregularity of 70% and were alkylated by us with ethyl bromide. Quaternization was carried out in 10% ethanol solution containing PVP (1 wt. % with fivefold excess of ethyl bromide) at 60 °C under inert N_2 atmosphere. The reaction was terminated by precipitation of the polymers into diethyl ether after variable times (~15 min, 2 h, or 12 h) to obtain 14%, 48%, or 100% alkylated pyridine units. These polymers, of the same degree of polymerization but different alkylation, are referred to below as Q14, Q48, and Q98. Their characteristics are given in Table I.

The inorganic salts (General Storage, pure grade, or Aldrich, purissium grade) were used as received after control experiments showed no difference if they were baked first at 600 °C to burn out conceivable organic contaminants. Deuterium oxide with 99.9% isotope content was obtained from Cambridge Isotope Laboratories and used without further purification. As a matter of terminology, when experiments were performed in D_2O rather than H_2O, we will refer to pD rather than pH.

The experiments were conducted under basic conditions, conditions where the silicon oxide carried a large intrinsic negative charge; pD $= 9.5$ for experiments involving dis-

TABLE I. Characteristics of the electrolyte chains.

Code	Degree of quaternization	M_w (g mol^{-1})	M_w/M_n^{b}	n_w^{b}
Q98	98%[a]	68 000	1.23	325
Q48	48%[a]	52 000	1.23	325
Q14	14%[a]	39 500	1.23	325

[a]Poly(1,4 vinyl)pyridine was quaternized in our laboratory by alklylation of PVP of $M_w = 34\,000$ to variable extents, as described in the text, after purchasing the uncharged polymer from Polymer Sources, Quebec, Canada.
[b]M_w and M_n denote weight-average and number-average molecular weight, respectively, and n_w denotes weight-average degree of polymerization.

placement of polymer Q48 by polymer Q98, and $pD = 10.5$ for experiments involving displacement of polymer Q14 by polymer Q98. Negative surface charge originated from hydrolysis of silanol groups on the oxide surface.

III. RESULTS AND DISCUSSION

The silicon oxide solid surface saturated with adsorbed PVP comprised a charge–charge complex of positively-charged polymer and negatively-charged solid surface.[1] The scheme of the exchange experiments was always similar; first one sample of polyelectrolyte was allowed to saturate the solid surface, then a second population of more densely charged chains is introduced into the aqueous solution. One should, at equilibrium, see complete displacement of the initially-adsorbed chains. We are interested in this paper to analyze a central experimental observation: the actual course of displacement was very slow.

For polymers in nonpolar solvents, it is known that the activation energy to desorb into pure solvent is prohibitively high,[18] but the situation is potentially more complex for adsorbed polyelectrolytes owing to the presence of salt ions which competes for surface sites. To begin with, we performed a control experiment which showed minimal desorption when polymer solution was replaced by pure salt solu-
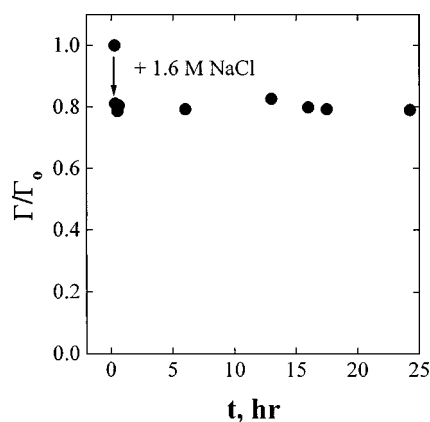

FIG. 1. Polymer Q48 (0.2 mg ml^{-1}) was allowed to adsorb onto the bare silicon oxide surface from 0.1 M NaCl at $pD = 9.2$, then the polymer solution was replaced by a buffer solution at much higher salt concentration, 1.6 M NaCl. After an expected immediate change in amount adsorbed the data showed no further desorption during the subsequent 24 h, showing that the larger desorption observed in the other figures of this study resulted from the presence of other polymer initially free in solution.

tion. In Fig. 1, mass adsorbed is plotted against time as the first polymer Q48 was allowed to adsorb onto the bare silicon oxide surface, next left adsorbed for 45 min under ''low salt'' conditions (0.1 M NaCl), then replaced by a buffer with 0.1 NaCl and finally by a buffer solution with very high salt concentration, 1.6 M NaCl. An immediate drop in mass adsorbed (by ~20%) was seen but the data display no subsequent desorption. The remainder of this paper discusses the enhanced desorption rates that we measured when exchange processes between surface and solution allowed desorbed chains to be replaced by newly-adsorbed chains, thus maintaining the surface coverage.

A. Net charge of adsorbed polymer

In this section we present data suggesting that the displacement process was regulated by the propensity of surface *charge* to remain constant—long after charge reached steady state, the surface coverage of individual polymer species continued to evolve.

A note about terminology. While it is certainly true that one should expect the actual charge of the polyelectrolyte chains to be lessened by counterion condensation,[19] no direct measurement of the actual charge was available so we will work with the available data, the degree of quaternization of the PVP samples. In extensive experiments we did seek to find perturbations in the infrared spectra that might indicate counterion condensation but no discernible perturbations of the infrared spectra could be discerned.

The near-constant surface concentration of charged (pyridinium) groups during the course of displacement is shown in Fig. 2(a) for the displacement of Q48 by Q98 and in Fig. 2(b) for the displacement of Q14 by Q98—both experiments refer to conditions where the ionic strength was relatively high for the respective sample. In these graphs the mass adsorbed of charged segments is plotted against elapsed time under conditions specified in the figure caption. When the displacer solution was introduced into the adsorption cell, the level of adsorbed increased by only ≈10% and remained at this same level for the subsequent 60 h.

A more conventional way to consider these exchange processes would be to analyze the total mass adsorbed. Total mass adsorbed is plotted against time in Fig. 3. Figure 3(a) shows the displacement of Q48 by Q98 and Fig. 3(b) shows the displacement of Q14 by Q98. One sees that the total mass adsorbed diminished during the exchange process. The reason is clear. For electrostatically-driven adsorption, less mass of the polyelectrolyte adsorbed, the higher its charge density, since uncharged units in the polyelectrolyte chain will then contribute proportionately less to the total amount adsorbed. This representation of the data appears to be less fundamental than the expression in terms of charge adsorbed; the data lack the attractive symmetry of Fig. 2.

In this range of ''high'' salt concentrations the exchanging polycations did not cause significant overcharge of the adsorbed layer; we consider below the cases of lower salt concentration. (Note, also that the criterion of whether salt concentration was low or high depended on the polymer's
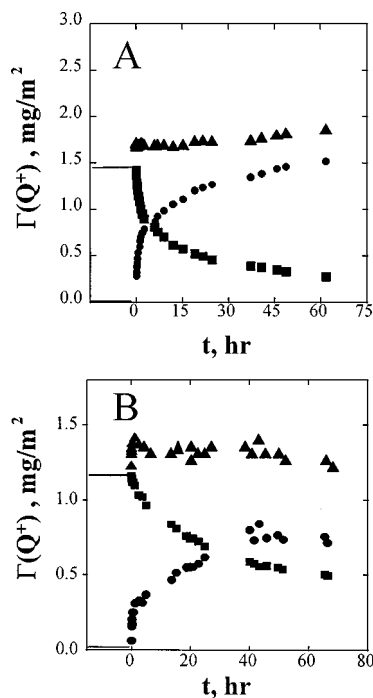
FIG. 2. Mass adsorbed of charged PVP units (the mass of pyridinium rings) is plotted against elapsed time for the displacement of Q48 by Q98 (a) and for the displacement of Q14 by Q98 (b). In (a) first Q48 (0.2 mg mℓ^{-1}, in 0.1 M NaCl at pD=9.2) was allowed to adsorb onto initially-bare silicon oxide for 45 min, then the polymer solution was replaced momentarily by the pure buffer at this pD, and finally this solution was replaced by Q98 (0.2 mg mℓ^{-1}) in the same buffer solution but at 1.3 M NaCl. In (b) first Q14 (0.2 mg mℓ^{-1}, in buffer solution without added salt) was allowed to adsorb onto initially-bare silicon oxide for 45 min, then the polymer solution was replaced momentarily by the pure buffer, and finally this solution was replaced by Q98 (0.2 mg ml^{-1}) in the same buffer solution but at 0.01 M NaCl. Symbols: squares, initially-adsorbed polymer; circles, incoming polymer; triangles, total mass adsorbed of charged pyridinium. The mass adsorbed to the initially-bare surface is indicated by the bold horizontal line at negative times. Time zero is when the adsorption cell was filled with displacer polymer solution.

charge, as will become evident from Figs. 12 and 13.) Our interpretation is that intermediate states, in which invading molecules adsorbed before previously-adsorbed molecules had been expelled, contributed little to the total charge adsorbed. In this regime of salt concentration the exchange of chains at the surface was relatively fast and charge regulation within the surface layer prevailed.

The behavior was somewhat different for experiments conducted at lesser salt concentration. Again a plateau level of charge was attained, but the magnitude increased after introducing the displacer polymer. In Fig. 4, adsorbed charge is plotted against time for the displacement of Q48 by Q98 at ''low salt'' [0.1 M NaCl, Fig. 4(a)] and ''medium salt'' conditions [0.7 M NaCl, Fig. 4(b)]. Note that the enhancement of adsorbed charge upon introducing the displacer polymer was larger, the lower the ambient salt concentration (50% increase at ''medium salt'' but almost 100% increase at ''low salt''). The surface composition of the two polyelectrolyte species continued to change for many hours in the ''medium salt'' regime but remained almost stuck at ''low salt'' concentrations. The rise in surface charge thus correlates with a tendency towards long-lived metastable states of surface composition.
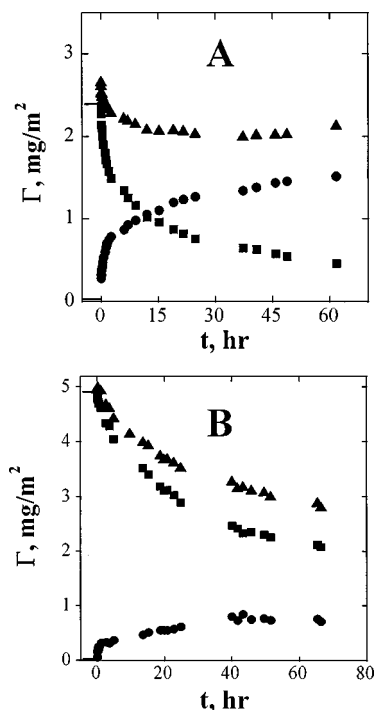

FIG. 3. Same experiments as in Fig. 2 except that the *total* mass adsorbed is plotted against elapsed time for the displacement of Q48 by Q98 (a) and for the displacement of Q14 by Q98 (b) under the conditions in the caption of Fig. 2. Symbols are the same as in Fig. 2.

The same tendency was found for our sample of lower charge density. In Fig. 5, adsorbed charge is plotted against time for the displacement of Q14 by Q98 in the presence of the buffer alone (no added NaCl). The enhancement of adsorbed charge was larger than for higher salt concentration
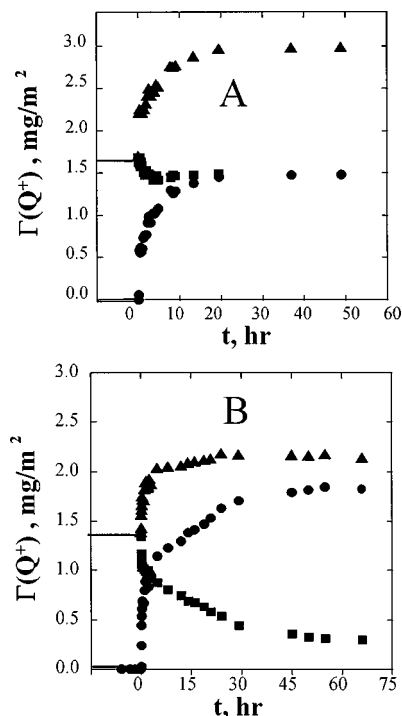

FIG. 4. Mass adsorbed of charged PVP units (the mass of pyridinium rings) is plotted against elapsed time for the displacement of Q48 by Q98 in 0.1 M NaCl (a) and 0.7 M NaCl (b) under the conditions in the caption of Fig. 2. Symbols and solution conditions in (a) are the same as in Fig. 2.
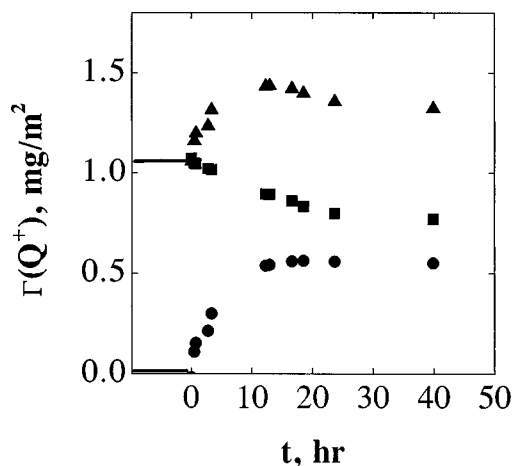
FIG. 5. Mass adsorbed of charged PVP units (the mass of pyridinium rings) is plotted against elapsed time for the displacement of Q14 by Q98 in buffer alone (no added NaCl) under the conditions in the caption of Fig. 2. The ionic strength of buffer was 3 mM to produce $pD=9.2$. Symbols are the same as in Fig. 2.

"low salt"

"medium salt"

"high salt"

FIG. 6. Schematic comparison of adsorbed chain configurations at ionic strength from ''low'' to ''high'' during intermediate states when invading molecules (shown as thick lines) and previously-adsorbed molecules (shown as thin lines) coexist in the adsorbed state. At low and medium salt concentrations the invading chains are only loosely attached to the surface and possess a relatively extended conformation. This may cause the charge on the solid surface to be overcompensated by adsorbed polyelectrolyte.

[Fig. 2(b)]. The data also suggest a transient small overshoot of adsorbed charge. Qualitatively, this corresponds to the ''medium salt'' regime observed for displacement of Q48 by Q98 molecules and will be discussed below.

The growth of the total charge in the adsorbed layer may be tied to the concentration (or lifetime) of ''overcharged'' intermediate states. The data show that slower exchange kinetics correlated with relatively frozen states of surface compensation and larger increase of the charge of polymer on the surface. More charge was adsorbed from accretion of invading molecules, than was displaced by the loss of previously-adsorbed molecules. While it might be argued that this proposed accumulation of the excess positive charge in the adsorbed layer might be electrostatically unfavorable, this seems inconsistent with the observation that the largest overcharge was observed for an ionic strength with Debye length 1 nm (exchange of Q48 by Q98 in 0.1 M NaCl). Otherwise stated, the surface became overcharged except at the very highest salt concentrations.

According to this scenario, Fig. 6 shows a hypothetical sketch of the possible composition of the adsorbed layers in these three schematic regimes. During the intermediate states when invading molecules and previously-adsorbed molecules coexist in the adsorbed state, invading molecules are loosely bound. The relatively large number of segments dangling into the solution contributes additional net positive charge at the surface. Also for neutral molecules, the possibility that invading chains possess a more extended conformation than at equilibrium has been proposed;[20,21] for polyelectrolyte chains, which bind so strongly at the segmental level, these intermediate states seem to be extremely long-lived. The data suggest that by this mechanism, electrical charge brought to the surface by invading chains should be larger, the lower the salt concentration. In the section below concerning the magnitude of surface charge, this hypothesis is shown to be consistent with classical measurements of the zeta potential of colloidal particles.
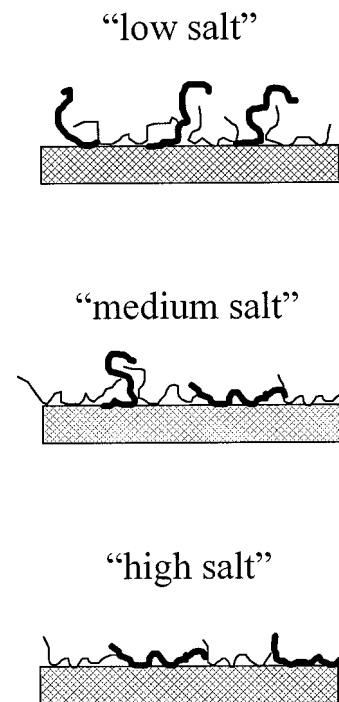
1. Contrast with the influence of ionic strength on screening

There is a slow polyelectrolyte exchange when the salt concentration is usually explained by considering the significance of electrostatic repulsion between invading chains and adsorbed layer.[6,22–25] The incomplete exchange of polyelectrolytes at low ionic strength is commonly explained by the buildup of repulsive electrostatic barriers during the exchange.[7,22–26]

However the effects found in this paper would be difficult to explain as just a consequence of charge screening. Figures 3, 4, and 5 show large differences according to the charge density of the previously-adsorbed chains (Q14 and Q48); though considerable displacement of Q14 took place at low ionic strength, salt concentrations above 0.2 M NaCl were required to produce equivalent displacement of Q48 molecules. At concentrations of salt as high as 0.1 M—a point where the Debye screening length was already 1 nm and consequently long-range electrostatic repulsion could not be argued—Q48 was still kinetically frozen.

Since the ease of the detachment of the macromolecular chains depends on the number of segmental contacts with the surface (note, parenthetically, that the same argument applies to the molecular weight dependence of the desorption of neutral macromolecules[27]), Q48 molecules would not detach from the surface at the same low ionic strength as Q14. At much higher ionic strength, Na^+ ions (whose charge is the same as the polymer segments), compete increasingly with the polymer segments for surface adsorption sites, as dem-

onstrated in our accompanying paper (preceding paper in this journal). They disrupt an increasingly large portion of contacts that the polyelectrolyte molecule makes with the surface, and detachment of Q48 molecules speeds up. Taken together, these data thus show the strong influence of ionic strength on modulating the intensity of sticking to the surface.

2. Magnitude of surface charge

The magnitude of the adsorbed charge turns out to be close to the expected density of negative units on the solid surface. For adsorption onto the initially-bare surface, the numbers of ≈ 1.4 mg m^{-2} [Fig. 2(a)] and ≈ 1.2 mg m^{-2} [Fig. 2(b)] are equivalent to 25 and 30 Å^2 per charged unit, respectively. The maximum charge density of ionized SiOH on a silica surface is reported to be similar, in the neighborhood of 20 Å^2–25 Å^2 per surface SiO$^-$ group.[28]

Several points of qualification must be mentioned here. First, adsorption of the polymer was probably also influenced slightly by residual roughness of the Si crystals (though roughness was measured by profilometry to be not larger than 15 Å in the direction perpendicular to the crystal surface). Second, these estimates are limited by the fact that at the present time we have no way to measure the population of inorganic ions in these surface layers. Third, we have not attempted in this discussion to take into account counterion condensation.

How then will we reconcile the observed empirical regularities, shown in this section, with these points of quantification? It might be that these subtleties affect the total charge on the solid surface and within the adsorbed layer to similar extents. Certainly, despite the provisos, it is fascinating to see that charge on the solid surface was approximately balanced by the opposite charge introduced by the adsorbed polymer. We have not yet attempted to make direct measurements of the sign or magnitude of the surface charge. In future work it would be desirable to have some direct measure of the net charge on the surface, perhaps by surface forces or atomic force microscopy measurements. However it is known, from zeta potential measurements on aqueous colloids, that the surface charge is overcompensated by the layer of adsorbed polyelectrolyte and increases with increasing concentration of polyelectrolyte in solution.[2,29]

B. Quantitative kinetics of adsorption and desorption

We saw in the previous section that except at the highest ionic strength, surface composition would adjust for a period of time and then cease to change, indicating some kind of kinetic arrest. This effect was more prominent, the lower the salt concentration. In this section, to further explore the point, we present additional data over a wider range of ionic strength.

Figure 7 compares the rate of accumulation of Q98 into previously-adsorbed Q48. While it is true that somewhat higher adsorbed amounts were obtained at 0.2 and 0.3 M than when the ionic strength was both lower and higher, this second-order effect is probably due to some kind of complex tradeoff between the driving forces for adsorption and de-
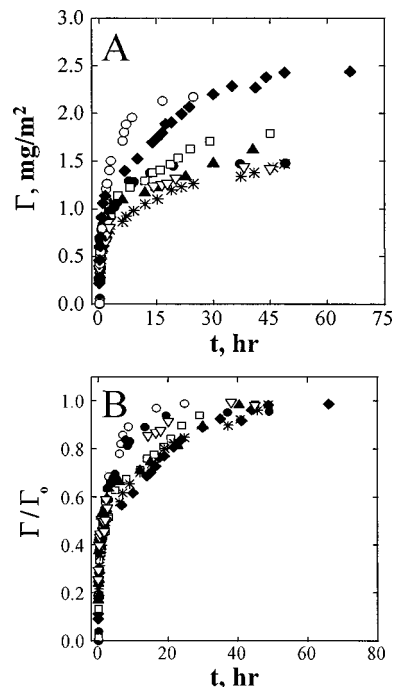

FIG. 7. Adsorption kinetics at various salt concentrations for the adsorption of Q98 after exposure to previously-adsorbed Q48 under conditions specified in the caption of Fig. 2. The relative mass adsorbed of Q98, $\Gamma(t)$, is plotted against time after introducing the displacer solution (a) or after normalization by Γ_0, the adsorption at the longest measurement time, $\sim$40–60 h (b). Filled circles, 0.1 M NaCl; open circles, 0.2 M; filled diamonds, 0.3 M; open squares, 0.7 M; filled up triangles, 1 M; stars, 1.3 M; open down triangles, 1.6 M NaCl.

sorption. The overall tendency is clear; the adsorption rate of the invading Q98 molecules depended only slightly on the ionic strength. This conclusion is evident from comparing the time dependence of mass adsorbed [Fig. 7(a)]; the data for different ionic strength all show the same general magnitude and time dependence. More quantitative regularity becomes evident when these data are normalized by the adsorbed amount at the longest measurement time [Fig. 7(b)]. The data then split into two families of curves; those in which the process was relatively rapid ($<$0.7 M NaCl) and those in which it was slower ($\geq$0.7 M NaCl).

The concomitant desorption kinetics showed larger differences. The raw data are summarized in Fig. 8; relative mass adsorbed is plotted against time after exchange. At the smallest ionic strength a small amount (only 10%) desorbed quickly, without subsequent change; the data are reminiscent of desorption into a solution of salt alone (see Fig. 1). But more and more polymer desorbed as the salt concentration was increased, and continued to do so for longer and longer times before reaching a state of kinetic arrest. Though the amount of incoming polymer (see Fig. 7) was similar at the highest and lowest salt concentrations, the amount of polymer displaced from the surface in the former case was 8 times larger. We interpret this to signify that the rate-limiting step in the displacement process was detachment, rather than penetration into the initially-adsorbed layer. The interpretation is consistent with the conclusion in the previous section, the strong influence of ionic strength in modulating the intensity of segment-surface adsorption.
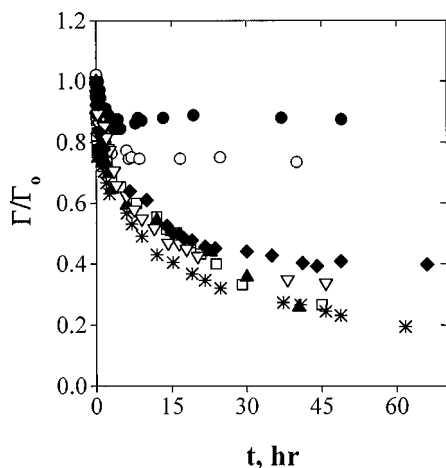
FIG. 8. Normalized desorption kinetics of Q48 by Q98 under the conditions specified in the caption of Fig. 2. The relative mass adsorbed of Q48, $\Gamma(t)/\Gamma_0$, is plotted against time after introducing the displacer solution. The normalization is to the mass adsorbed just before introducing the displacer solution. Symbols are same as in Fig. 7.

FIG. 10. Same data as in Fig. 8 but plotted logarithmically against square root of time. One observes that a linear relationship held for longer times, the higher the salt concentration. The desorption of Q14 by Q98 could be described in this way with a similar degree of success (not shown).

Now we turn to quantitative analysis of the desorption kinetics. We were unsuccessful in fitting these data to an exponential relationship. The data showed curvature (as shown in the semilogarithmic plot in Fig. 9), indicating that desorption was slower than exponential from the start. Thus the data were inconsistent with the first-order process that, for nonpolar polymers, has sometimes been suggested.[20,30,31] Better success was obtained in fitting these observations to a functional form exponential on the square root of elapsed time. Figure 10 shows that the data are broadly consistent with a linear dependence of logarithmic mass adsorbed on $t^{1/2}$ for the initial 1–2 h (but not during the initial 5–10 min). This dependence persisted to longer times, the higher the ionic strength. For the highest ionic strength, the $t^{1/2}$ dependence persisted for the entire span of the experiment, 60 h.

Motivation for a functional dependence of exponential in $t^{1/2}$,

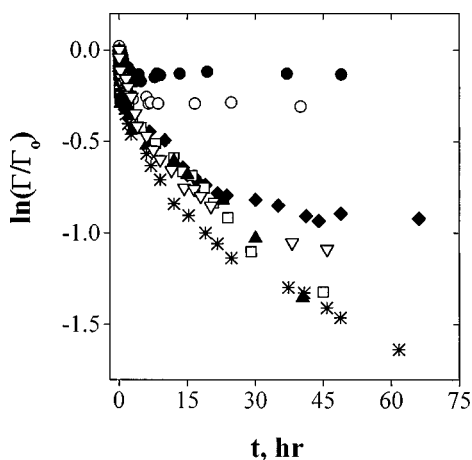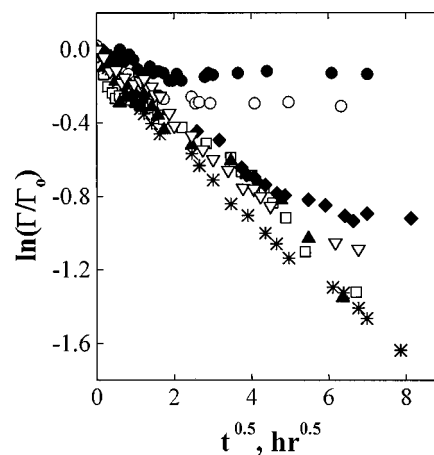$$\Gamma(t)/\Gamma_0 \sim \exp[-t/\tau_{\text{off}}]^\beta, \tag{1}$$

FIG. 9. Same data as in Fig. 8 but plotted semilogarithmically. Unlike the representation in Fig. 9, all the data display substantial curvature.

with $\beta \approx \frac{1}{2}$ comes from experiments in which the desorption of nonpolar homopolymers was studied[12] and a simple theory which predicts $\beta = \frac{1}{2}$ if desorption is rate-limited by diffusion away from the surface through other adsorbed chains rather than energetic detachment.[13] Here, $\Gamma(t)$ denotes time-dependent mass adsorbed and Γ_0 denotes its value before initiation of exchange. The desorption of Q14 by Q98 could be described in this way with a similar degree of success (not shown). Though the comparison to Eq. (1) must be considered to be tentative since the implied time constant would be of order 25 h,[32] which exceeds the time that entered the actual fit of the data, agreement as concerns the value of β is pleasing.

Obviously, an alternative explanation for desorption slower than exponential could be constructed by assuming that desorption is rate-limited by detachment of chains but that the surface from which they desorb is heterogeneous; a process that is the result of exponential rates with a spectrum of time constants appears, in sum, to be slower than exponential. But we know of no fundamental reason that heterogeneity should produce the particular value that we observed by a fit to Eq. (1), $\beta = \frac{1}{2}$. Instead, the satisfactory success of this functional form suggests that desorption in this polyelectrolyte system was diffusion-controlled during the initial stages.[13] The effect of increasing the ionic strength was mainly to raise the fraction of initially-adsorbed polymer that could be displaced—not to modify the short-term desorption kinetics.

C. Further discussion of adsorption heterogeneity

We argued in the previous section that adsorption heterogeneity is an unlikely explanation for the relatively rapid desorption observed when the displacer polymer was first introduced into solution. Now we consider the kinetic arrest that was observed at longer times (except at the highest ionic strength).

Uncharged polymers show similar behavior. One subpopulation of initially-adsorbed chains desorbs relatively quickly and a second subpopulation is so much slower to be
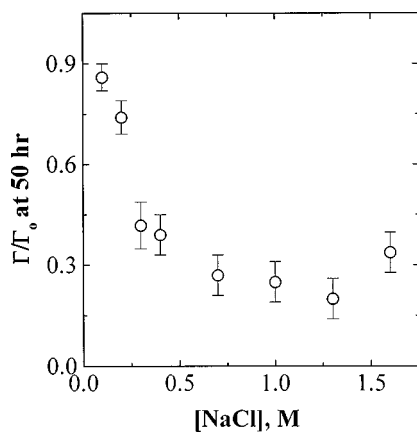
FIG. 11. Surviving fraction of Q48 at $\approx$50 h, plotted against molar concentration of NaCl for the displacement of Q48 by Q98 under the conditions described in the caption of Fig. 2.

FIG. 12. Dichroic ratio (D) of the pyridine ring of Q14 centered at 1604 cm^{-1}, plotted against mass adsorbed of Q14 as it was progressively displaced by Q98 during exchange experiments under conditions specified in the caption of Fig. 2. The error bar reflects repeatability of the absolute magnitude in independent experiments; relative measurements are more precise.

desorbed that it appears to be kinetically trapped. This has been described for polymer displacement in many systems provided that the solvent quality is better than the theta solvent; for displacement of polystyrene by polymethylmethacrylate,[33] by polyisoprene,[34] and even by a weakly adsorbing polymer, deuterio polystyrene.[35] Those observations have been interpreted to signify that the initially-adsorbed polymer adsorbed with a broad distribution of substrates. Chains that were adsorbed relatively weakly could be displaced by a given driving force of displacer polymer in solution, but those that were adsorbed more strongly could not be.[36] Endemic heterogeneity of the adsorbed layer was also recently found for polyelectrolytes.[37,38]

The fractional surface population of initially-adsorbed polymer that survived on the surface 50 h after exchange of the ambient solution is plotted in Fig. 11 against molar concentration of NaCl. As the salt concentration was increased, the survived fraction decreased from near unity (desorption into buffer solution) to much smaller levels and since the desorption for the highest salt concentrations followed the stretched exponential form up to the latest accessible time (60 h) we suppose that in this case no portion will be trapped at longer times than this. Elsewhere we have analyzed similar data for nonpolar polymers and have argued that the fraction survived decreases with increase of the displacement driving force.[39] Here, displacement driving force is constant and we vary binding energy by adding the competing Na$^+$ ions, which disrupt polymer contacts with the surface and screening of electrostatic interactions.

Seeking to acquire more direct evidence of heterogeneity than just presented, additional analysis was made of the anisotropy of pyridine segments on the adsorbed chains. From measurements of the infrared absorbance of a vibrational band in p and s polarization directions (A_p and A_s, respectively), the dichroic ratio can be defined as the ratio, $D \equiv Ap/As$.[40,41] For the refractive indices relevant to this system, $D = 2.05$ expresses isotropy and $D < 2.05$ denotes a dichroic ratio such that the pyridine ring lies preferentially parallel to the solid surface. It proved to be impossibly difficult to definitively resolve the infrared dichroism of Q48 and Q98, but for the displacement of Q14 the measurement was
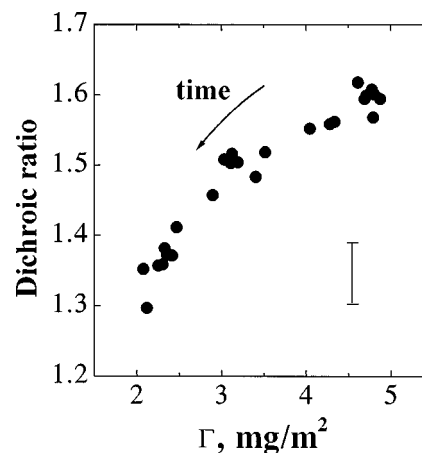
successful. Here we focus on anisotropy of the uncharged pyridine ring, whose relatively intense signal was not significantly masked by overlap with signal from the displacer Q98.

Figure 12 shows dichroism of the pyridine ring plotted against mass adsorbed of Q14 during the time that it was displaced by Q98. One sees that the residual polymer grew increasingly anisotropic as more and more was displaced. This again suggests that the adsorbed chains possessed an inhomogeneous conformational distribution; the less anisotropic chains were desorbed first.

Finally, we report an interesting effect of solvent quality. Figure 13 shows the magnitude of the fraction survived to long times (70 h) plotted against molar concentration of NaCl for the displacement of Q14. One sees in this case a pronounced minimum in the fraction survived. At the still larger ionic strength of 0.05 M NaCl, the sample of Q14 of this concentration precipitated from solutions; this is the "salting-out" effect that is well-known.[42] The minimum thus seems to signal the onset of worsening of quality of the
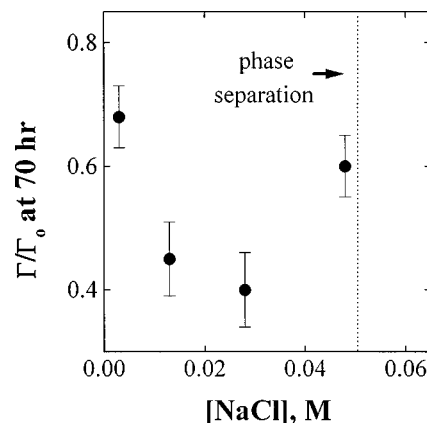

FIG. 13. Surviving fraction of Q14 at $\approx$70 h, plotted against molar concentration of NaCl for the displacement of Q14 by Q98 under the conditions described in the caption of Fig. 2.

solvent as phase separation was approached, and this effect set in when the salt concentration was still far below the point of insolubility. The data suggest that changes in solvent quality, as the salt concentration is raised, may have a profound influence on adsorption and exchange of polyelectrolytes at surfaces. The effect should be general since most organic polyelectrolytes may be considered to be a copolymer of polar charged units and hydrophobic uncharged units. In contrast to widely discussed salt effects on the screening length that are often considered, this is, to the best of our knowledge, the first report of salt-induced impending insolubility on polyelectrolyte desorption and exchange kinetics.

IV. OUTLOOK AND CONCLUSIONS

A novel feature of this investigation was the *in situ* measurement of surface composition during long equilibration periods as polyelectrolyte chains adsorbed and desorbed in competition with one another. We believe that the FTIR-ATR techniques used here for this purpose could also find wide applicability in a variety of other aqueous systems. However, for many applications it would be desirable to find polymers with vibrational bands that show significant absorptivity solely along the chain backbone. The orientation of the chain relative to the surface could then be studied,[43] not just the orientation of the side-chains that we have addressed here.

Upon challenging the initially-adsorbed layer by a solution of the same polymer whose charge density was higher, we should eventually expect to see complete displacement of the initially-adsorbed chains; partly owing to the vast excess of chains in solution relative to those at the surface, and partly owing to the higher charge density (hence the higher sticking energy) of the displacer chains. Since the invading Q98 molecules had at least 2 times more charged groups per chain, they adsorbed more strongly regardless of the ionic strength. But a view of this kind is predicated on the achievement of full equilibrium. One of the central qualitative conclusions from this study is that metastable nonequilibrium states are extremely long-lived. We have sought, in this study, to explore the patterns of adsorption–desorption on the way to this kinetically-arrested state.

The problem, after the chains in solution were switched to others that adsorbed more strongly, was for invading chains to penetrate the previously-adsorbed layer, and conversely for previously-adsorbed chains to wend their way out. The data presented above suggest that the former process was more rapid than the latter. Theoretical attention has been given, for nonpolar polymers, to the kinetic barriers for invading chains to penetrate a previously-adsorbed layer,[20,30] but little yet to the kinetic barriers for desotion, with the exception of tentative proposals.[13,44] It is not self-evident to us that desorption must necessarily be rate-limiting—given the large electrostatic repulsion for charged chains from solution to approach charged adsorbed chains—but it was the experimental finding. Evidently the barriers presented by electrostatic repulsion, as invading chains approached the surface, were less than those for desorption itself.

The intermediate state ensued in which invading chains from solution had achieved a toehold on the surface, but had not yet displaced those previously-adsorbed. Little is known so far about chain configurations in this state (dichroism of chains with strong infrared-active vibrations along the chain backbone may eventually provide a way to address the question experimentally), but obviously the process at work was unzipping of initially-adsorbed chains from the surface. This problem, of electrically-charged units in intimate contact with a solid surface, was in another scientific age known as the ''Stern layer.'' It seems to be the essence of the problem of displacement kinetics that involve polyelectrolytes.

We have speculated in this study that the intermediate states may carry enhanced positive charge because they consist of molecules more extended from the surface than the initially-adsorbed chains. This would explain the observed higher overcharge at the lowest ionic strengths, where less exchange occurred.

Another theme that has emerged from this study is that the total amount adsorbed appeared to mask a broad distribution of adsorption substates. The data show clearly that some portion of the desorbing polymers could be detached and that a second portion was irreversibly adsorbed, but that this latter portion decreased with increase of the salt concentration. It thus appears that the fraction irreversibly adsorbed represented a tradeoff between the intensity of adsorption and the intensity of the driving force for desorption. The effect of increasing the salt concentration was to reduce the former and to increase the latter.

In this scenario, the decrease of survival fraction with increasing salt concentration reflected the intensity of disruption of polymer bonds with the surface by small ions and further reflected an energetic landscape of the adsorbed Q48 molecules. The functions of changing the salt concentration were at least three;

(1) To screen charges. It is traditional to consider this aspect of polyelectrolyte adsorption[7,25] but it seems not sufficient to explain the large differences that we observed when the salt concentration was so large as to expect near-complete screening.

(2) To disrupt the intensity of surface-segment attraction. The sticking energy of charged polyelectrolyte segments was reduced when small inorganic ions competed with it for surface access.

(3) To regulate the solvent quality. The chemical makeup of a polyelectrolyte chain is in part hydrophilic, in part hydrophobic. The aqueous solvent becomes a nonsolvent when the salt concentration is sufficiently large.

The theoretical literature on the problem of adsorption–desorption-exchange seems quite limited in comparison with the extensive literature on models of polyelectrolyte adsorption onto an initially-bare surface. Although dynamic problems are difficult we believe that more can be done to develop useful model systems by using dynamical exchange processes to probe questions that underly the assumptions of various equilibrium and nonequilibrium theories.

Many questions remain for future work. Among the most prominent are the extent to which polyelectrolytes generically display the patterns shown in this study—to what extent must one also worry about specific chemical influ-

ences? Could the desorption-exchange process produce surface compositions that are spatially inhomogeneous? What happens when the solution concentration of displacer molecules is larger than dilute—when essential aspects of charge screening enter the solution side of the equation as well as the physics of the adsorbed layer? Also very relevant to this problem are issues of knowing the flexibility of a polyelectrolyte chain. There has been much discussion of how flexibility may change with ionic strength, but it is usual for such analysis to consider chains at low concentration,[45] whereas the flexibility of chains in close proximity to other charged chains (while in a state of adsorption!) lies at the heart of the surface problem.

ACKNOWLEDGMENTS

[1] S. A. Sukhishvili and S. Granick, J. Chem. Phys. **109**, 6861 (1998), preceding paper.
[2] J. Meadows, P. A. Williams, M. J. Garvey, R. A. Harrop, and G. O. Phillips, Colloids Surf., A **32**, 275 (1988).
[3] E. Pefferkorn, A. C. Jean-Chronberg, and R. Varoqui, Macromolecules **23**, 1735 (1990).
[4] L. Ödberg, S. Sandberg, S. Welin-Klintström, and H. Arwin, Langmuir **11**, 2621 (1995).
[5] M. A. G. Dahlgren, H. C. M. Hollenberg, and P. M. Claesson, Langmuir **11**, 4480 (1995).
[6] D. R. Bain, M. C. Cafe, I. D. Robb, and P. A. Williams, J. Colloid Interface Sci. **88**, 467 (1982).
[7] A. W. M. de Laat, G. L. T. van den Heuvel, and M. R. Böhmer, Colloids Surf., A **98**, 61 (1995).
[8] L. Wågberg, L. Ödbreg, T. Lindström, and R. Aksberg, J. Colloid Interface Sci. **123**, 287 (1988).
[9] H. E. Johnson, J. F. Douglas, and S. Granick, Phys. Rev. Lett. **70**, 3267 (1993).
[10] J. D. Andrade and V. Hlady, Adv. Polym. Sci. **79**, 1 (1986).
[11] J. J. Ramsden, Chem. Soc. Rev. **24**, 73 (1995).
[12] H. E. Johnson and S. Granick, Science **255**, 966 (1992).
[13] J. F. Douglas, H. E. Johnson, and S. Granick, Science **262**, 2010 (1993).
[14] P. Frantz, D. Perry, and S. Granick, Colloids Surf., A **86**, 295 (1994).
[15] T. C. McGlinn, D. J. Kuzmenka, and S. Granick, Phys. Rev. Lett. **60**, 805 (1988).
[16] P. Frantz and S. Granick, Macromolecules **28**, 6915 (1995).
[17] P. Frantz and S. Granick, Langmuir **8**, 1176 (1992).
[18] G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman & Hall, London, 1993).
[19] G. S. Manning, J. Chem. Phys. **51**, 924 (1969).
[20] P.-G. de Gennes in *New Trends in Physics and Physical Chemistry of Polymers*, edited by L.-H. Lee (Plenum, New York, 1990).
[21] M. A. Cohen Stuart and G. J. Fleer, Annu. Rev. Mater. Sci. **26**, 463 (1996).
[22] U. S. Adam and I. D. Robb, J. Chem. Soc., Faraday Trans. 1 **79**, 2745 (1983).
[23] H. A. van der Schee and J. Lyklema, J. Phys. Chem. **88**, 6661 (1984).
[24] J. A. Wright, R. Harrop, P. A. Williams, G. Pass, and I. D. Robb, Colloids Surf., A **24**, 249 (1987).
[25] R. Ramachandran and P. Somasundaran, J. Colloid Interface Sci. **120**, 184 (1987).
[26] A. W. M. de Laat and G. L. T. van den Heuvel, Colloids Surf., A **98**, 53 (1995).
[27] J. F. Douglas, Macromolecules **22**, 3707 (1989).
[28] R. K. Iler, *Chemistry of Silica* (Wiley, New York, 1979).
[29] S. A. Sukhishvili, O. S. Chechik, and A. A. Yaroslavov, J. Colloid Interface Sci. **178**, 42 (1996).
[30] P.-G. de Gennes, C. R. Acad. Sci. Paris **301**, 1399 (1985); **302**, 765 (1986).
[31] E. Pefferkorn, A. Haouam, and R. Varoqui, Macromolecules **22**, 2677 (1989).
[32] Detailed analysis of the data in Fig. 10 (not shown) suggests a time constant $\tau_{off} \approx 24$ h (≥ 0.3 M NaCl) and roughly 5 times slower at lesser salt concentration.
[33] E. Enriquez, H. M. Schneider, and S. Granick, J. Polym. Sci., Polym. Phys. **33**, 2429 (1995).
[34] H. M. Schneider, S. Granick, and S. Smith, Macromolecules **27**, 4721 (1994).
[35] P. Frantz and S. Granick, Macromolecules **27**, 2553 (1994).
[36] H. M. Schneider and S. Granick, Macromolecules **25**, 5054 (1992).
[37] H. Tanaka, A. Swerin, and L. Ödberg, Langmuir **10**, 3466 (1994).
[38] N. G. Hoogeveen, M. A. Cohen Stuart, and G. J. Fleer, J. Colloid Interface Sci. **182**, 146 (1996).
[39] J. F. Douglas, H. M. Schneider, P. Frantz, R. Lipman, and S. Granick, J. Phys.: Condens. Matter **9**, 7699 (1997).
[40] S. Frey and L. K. Tamm, Biophys. J. **60**, 922 (1991).
[41] R. P. Sperline, Y. Song, and H. Freiser, Langmuir **8**, 2183 (1992).
[42] H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, Ch. Seidel, and D. Stscherbina, in *Polyelectrolytes: Formation, Characterization and Application* (Hanser, Munich, 1994).
[43] E. Enriquez and S. Granick, Colloids Surf., A **113**, 11 (1996).
[44] Y. Wang and R. Rajagopalan, J. Chem. Phys. **105**, 696 (1996).
[45] J.-L. Barrat and J.-F. Joanny, Adv. Chem. Phys. **19**, 1 (1996).